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Effect of skin contact on the antioxidant phenolics in white wine

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Abstract

A study was conducted to determine the effect of skin contact on the antioxidant phenolic composition and sensory properties of wine from Listán Blanco, a variety of *Vitis vinifera* grown in the Canary Islands. Compared with direct pressing of vintage, skin contact increased the levels of phenolics including those with physiological properties, and improved the sensory characteristics. The values of resveratrol and its glucoside isomers were the highest found so far in white wine.

Keywords: Skin contact; White wine; Phenolics

1. Introduction

Pomace or skin contact (maceration) is an alternative technique in making white wine. Thirty years ago, experiments were begun to study the differences in composition and quality with contact time of juice with skin and seed (Ough, 1969). The main interest was to generate the phenolics responsible for aged character without the additional tannin and astringency associated with the press fractions (Boulton, Singleton, Bisson & Kunkee, 1996). This technique has been widely researched since then, with diverse results (Arnold & Noble, 1979; Baumes, Bayonove, Barillère, Samson & Cordonnier, 1989; Cabaroglu, Canbas, Baumes, Bayonove, Lepoutre & Günata, 1997; Falqué & Fernández, 1996; Franco-Aladrén, 1993; Le Fur & Ferrari, 1990; Meurgues, 1996; Nicolini, Versini, Dalla, Barchetti & Menini, 1994; Ramey, Bertrand, Ough, Singleton & Sanders, 1986; Singleton, Zaya & Trouslade, 1980; Stephen, Noble & Schmidt, 1986). Depending on the grape cultivar employed, the temperature and time of contact give rise to considerable variation. In recent years, the aim has been to obtain wine with low astringency and browning potential but high aromatic intensity.

Most of this work has been focused on studying the volatile compounds and aromatic potential arising from skin contact (Arnold & Noble, 1979; Baumes et al., 1989; Cabaroglu et al., 1997; Falqué & Fernández, 1996; Nicolini et al., 1994; Ramey et al., 1986). One result has been the increase in flavour extraction from the skin. Moreover, there is greater extraction of phenolic components (Ramey et al, 1986; Singleton et al., 1980), which can contribute to the flavour of finished wine and may exert a positive health effect attributed to moderate wine consumption (Frankel, Waterhouse & Teissedre, 1995). Flavonoids increase slightly with contact time, but seem to increase strongly with the contact temperature. Below 10°C, the extraction of flavonoids is limited (Ramey et al., 1986). These compounds contribute to bitterness and astringency, and can act as oxidation substrates in white wine. The hydroxycinnamates are major phenolic components and can be both oxidation substrates and browning precursors (Singleton, Zaya, Trouslade & Salgues, 1984).

In general, increases in contact temperature and time seem to give finished wines with higher pH, potassium and total phenolics levels (Singleton et al., 1980; Stephen,

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Noble & Schmidt, 1986). Skin contact increases the amount of hydroxycinnamates, gallic acid and flavonoids (Singleton & Trouslade, 1983).

The aim of this study was to determine the influence of skin contact, in producing Listán Blanco wines, on the content of phenolics with physiological properties, and on their sensory characteristics.

2. Materials and methods

2.1. Grapes and winemaking procedure

The cultivar Listán Blanco is the most widely grown variety of *Vitis vinifera* in the Canary Islands (Spain) (more than 6000 ha). The grapes for this study were harvested at maturity (10.6 °Baume) during the 1998 season in the Valle de Güimar, mid-south east of the island of Tenerife. Healthy grapes (7000 kg) were harvested manually and transported to the Valle de Güimar experimental wine-production centre, and divided into two batches. One batch was treated in the standard way (control wine) with direct pressing of vintage in a membrane press; 40 mg/l of sulfur dioxide was added as metabisulphite; the juice was then settled at 15°C, adjusting the acidity of the must to pH 3.2 with tartaric acid. Pectic enzyme (3 g/100 l of Endozym Active), silica sol (1 ml/l of Baykisol) and gelatin (0.086 ml/l of Gelsol) were added. When the juice clarification was 20 NTU it was racked and inoculated with *Saccharomyces cerevisiae* (commercial yeast), then fermented at 15°C. During fermentation, 40 g/Hl of bentonite was added and the decrease in density was checked daily. At the end of fermentation all wines were racked, 50 mg/l of sulfur dioxide was added as metabisulphite, and they were stored in the tanks.

For the skin-contact batch, the process was as above except that the grapes were initially destemmed and crushed, macerated at 16°C for 24 h and then pressed horizontally.

2.2. Wine composition

Standard methods of analyses for general wine composition were used. Some volatile compounds present in the wine were analyzed by GC (Spanish Agriculture Ministry, 1985). The following spectrophotometric determinations were carried out: catechin (Pompei, 1971); Folin-Ciocalteu index (Regulation for wine of European Commuunity, 1990); browning test in oxidative medium (POM-test) (Schneider, 1995); absorbance at 280, 320 and 420 nm; and total phenolics index (Paronetto, 1979).

The phenolic compounds were determined by high perfomance liquid chromatography (HPLC) (Betés-Saura, Andrés-Lacueva & Lamuela-Raventós, 1996).

2.3. Sensory evaluation

All sensory analyses were perfomed by a panel of 10 judges with extensive wine-tasting experience. Two testing procedures were used. The triangular test where three glasses are presented and the panellist told that two contain the same wine and one is different, and a rated score card from the Spanish Ministry of Agriculture (1985), used to rate wines in the proper order: visual, odour, flavour, and integrated quality.

3. Results and discussion

3.1. Must and fermentation

At the beginning, the musts obtained by skin contact and control had similar values of total acidity (about 4.4 g/l as tartaric acid) and pH 3.45. After 24 h of skin-contact, these values changed to 3.7 g/l and pH 3.7, respectively. This fact reflects one disadvantage of pomace contact of a white cultivar with low acidity, such as Listán Blanco. It induces a greater extraction of potassium and consequently a decrease in total acidity and an increase in pH. These differences were corrected with addition of tartaric acid. Even so, after fermentation, the pH of the skin-contact wine was 0.1 units higher than the control wine. The fermentation kinetics were similar in both cases.

3.2. General wine composition

The wine made with skin-contact had lower values for alcohol and total titratable acidity, and higher values for pH and extract (Table 1), as reported in previous studies (Cabaroglu et al., 1997).

3.3. Volatile compounds

In Table 2, some volatile compounds are presented. The most significant difference appears in the higher methanol content in skin-contact wine, due to longer

Table 1
Chemical analysis of Listán Blanco wines

	Control wine	Skin-contact wine
Density (20°/20°)	0.9928	0.9942
Ethanol (%,v/v)	11.05	10.40
Extract (g/l)	19.30	20.30
Reducing sugars (g/l)	1.0	1.0
Volatile acidity as acetic acid (g/l)	0.14	0.15
Total acidity as tartaric acid (g/l)	5.48	4.40
PH	3.37	3.44
Malic acid (qualitative)	NO	NO

Table 2
Mean values for some volatile compounds (mg/l)

	Control wine	Skin-contact wine	Significance level[a]
Acetaldehyde	22.6	31.2	*
Ethyl acetate	20.7	24.2	ns
Methanol	19.9	53.2	**
2-Butanol	ND	ND	
1-Propanol	12.6	16.1	*
Isobutanol	12.4	16.3	*
1-Butanol	ND	ND	
Isoamyl and amyl alcohol	39.6	52.7	ns

[a] Significance at which means differ as shown by two sample analysis; *, **, denote significances at $P<0.05$ and $P<0.01$ respectively; ns: not significant.

contact between pectins and natural pectin methylesterase. The quantity of higher alcohols was increased.

3.4. Spectrophotometric determinations

The values were, in general, higher in the skin-contact wine than control wine (Table 3). The absorbance units in the area of the hydroxycinnamates at 320 nm, and the total phenols at 280 nm, were higher in the skin-contact wine than the control. These results were confirmed by HPLC. They demonstrate a greater extraction of flavonoid and non-flavonoid compounds due to maceration. The POM test was positive for both samples. This tendency to oxidation was slightly higher in the skin-contact wine.

3.5. Phenolics content

The results from quantification of the individual phenolic compounds (Table 4) are very high, e.g., in the skin-contact wine, the sum of *cis* and *trans* resveratrol and their glucosides, the piceids, gives a total of 5.18 mg/l; to our knowledge, this is the highest level described in white wines, since the average level in Spanish white wines is 0.480, with a maximum value of 1.24 mg/l (Romero-Perez, Lamuela-Raventos, Waterhouse & Torre-Boronat, 1996). These two substances have recently been related to beneficial effects on humans (Frankel, Waterhouse & Kinsella, 1993; Leighton, Urquiaga & Diez, 1998) as has quercetin (Bravo & Bravo, 1997; Goldberg, Tsang, Karumanchiri & Soleas, 1998) which increased 8-fold in the skin-contact wine to a value of 8 mg/l, which is similar to and in many cases superior to commercial red wines from all over the world (Goldberg et al., 1998). The skin-contact wine presents phenol values higher than the control and most well-known white wines. Only tyrosol did not present significant differences, since it is produced from tyrosine by yeast during fermentation and is the only phenolic compound produced in significant amounts from non-phenolic precursors. The high level of flavonoids in the skin-contact wine was expected since these compounds are located mainly in the skin of grapes. Thus, catechin increased 4-fold and total flavonoids from 3.11 to 16.5 mg/l. Non-flavonoids were also extracted in greater quantity in the skin-contact wine. For example, the 115 mg/l of *trans*-caftaric acid in the skin-contact wine as against the 65 mg/l in control wine is notable.

In both types of wines, hydroxycinnamates were the major phenolics (85% of the total phenol quantified in control wine and 91% in skin-contact wine), as reported in previous studies (Betés-Saura et al., 1996; Singleton & Trouslade, 1983). *trans*-Caftaric acid was found at the highest level, ranging from 65.7 mg/l in control wine to 116 mg/l in skin-contact wine. *trans*-Coutaric and *cis*-coutaric acid were at the second highest concentration, and their levels ranged from 8.72 to 38.2 mg/l. *trans*-Ferulic acid was present at a lower concentration (0.28 mg/l), *cis*-caffeic was not detected.

Benzoic acids increased 100% with pomace contact. Protocatechuic increased from 5.37 to 10.7 mg/l and gallic acid increased 5-fold, as it is mainly located in the seeds. In the control wine, the flavonoid group was the minority, i.e. only 2% of total analyzed phenol. In the skin-contact wine they represented only 6.7%.

Certain phenols can act as precursors of enzymatic oxidations in the must and later autocatalytic oxidation in wine. These phenomena can give rise to more intense golden hues, and what is worse, production of brown polymers. The hydroxycinnamates (caftaric and coumaric acid) and some flavonoids like catechin seem to play a role in this as oxidation precursors. The skin-contact wine seems to oxidize more easily than the control, as observed in the oxidation test. However, the 2-*S*-glutathionylcaftaric acid that originates during enzymatic oxidation in the must, is at a lower level in the

Table 3
Spectrophotometric determinations

	Control wine	Skin-contact wine	Significance level[a]
Catechin (mg/l)	9.5	37.1	**
Folin-ciocalteu index	6.39	7.75	ns
AU 420 nm	0.116	0.137	ns
POM-test	0.132 (14%)	0.164 (20%)	*
Total phenolic index (280 nm) mg/l catechin	587	867	**
AU 280 nm	10.63	13.77	*
AU 320 nm	10.06	14.86	*

[a] Significance at which means differ as shown by two sample analysis; *, **, denote significances at $P<0.05$ and $P<0.01$ respectively; ns: not significant.

Table 4
Mean values for some phenolic compounds (mg/l)

	Control wine	Skin-contact wine	Significance level[b]
Gallic acid	0.63	3.20	**
Protocatechuic acid	5.37	10.7	**
Tyrosol	8.16	7.14	ns
Catechin	2.11	8.38	**
cis-Piceid	1.09	2.70	*
cis-Resveratrol	0.04	0.60	**
cis-Caftaric acid	3.32	4.40	ns
trans-Caftaric acid	65.7	116	*
2-*S*-glutathionylcaftaric	6.87	4.94	ns
cis-Coutaric acid	23.2	38.2	*
trans-Coutaric acid	8.72	36.58	**
cis-Caffeic acid	ND	ND	
Fertaric acid	1.17	1.74	**
trans-Caffeic acid	8.21	6.10	ns
Coumaric acid	2.90	3.36	ns
Ferulic acid	0.28	0.41	*
trans-Piceid	0.33	1.26	**
trans-Resveratrol	0.22	0.62	*
Quercetin-3-glucuronide	1.00	8.07	**
Total phenolics[a]	132	247	*
Total hydroxycinnamics	120	211	*
Total flavonoids	3.11	16.5	**
Total benzoic acids	6.36	13.9	**
Total resveratrol and piceid	1.68	5.18	*

[a] Data obtained without tyrosol value.
[b] Significance at which means differ as shown by two sample analysis; *, **, denote significances at $P<0.05$ and $P<0.01$ respectively; ns : not significant.

skin-contact wine. This compound can give rise, by chemical oxidation, to polymers of reddish-brown colour, and is present in higher quantities (4.94 to 6.87 mg/l) than those described in wines produced with other cultivars (Betés-Saura et al., 1996).

3.6. Sensory evaluation

The triangular taste test used to distinguish the two types of wine, gave a significant difference ($P<0.01$). These wines were easily distinguishable by the tasters. Applying the rated score card of the Spanish Ministry of Agriculture, the best score was reached by the skin-contact wine, showing a higher aroma intensity.

4. Conclusions

The Listán Blanco wines in this study present very high values of phenolic compounds considered beneficial to human health. The skin-contact wine registers the highest resveratrol and piceid values found so far in a white wine. Skin contact can therefore improve physiological properties and sensory characteristics of white wine.

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